

XRF analysis of high gain-on-ignition samples by fusion method using fundamental-parameter method

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Fusion bead method produces homogeneous samples and is suitable for analysis using fundamental-parameter (FP) method in XRF. This report describes an FP method for analysis of non-oxide samples such as metals made into fusion beads. During the fusion process, all non-oxide elements in the sample are oxidized and gain-on-ignition (GOI) occurs. Volatile elements such as carbon do not remain in the sample as a result of fusion. This process is known as loss-on-ignition (LOI). To obtain reliable analysis results of fusion beads with the FP method, weight changes as a result of LOI and GOI must be reflected accurately in software calculation. The newly developed FP method, which takes these weight changes and dilution ratios into consideration, was able to yield accurate analysis results for ferroalloys FeSi, FeMn, and SiMn, some of which have high carbon content. This method is also applicable for sulfides and carbides. © 2013 International Centre for Diffraction Data. [doi:10.1017/S0885715613000304]

Key words: XRF, fusion bead method, fundamental-parameter method, GOI, LOI, ferroalloys

I. INTRODUCTION

The fusion bead method is an effective means to remove inhomogeneities in powder samples such as mineralogical and grain size effects, which can cause analysis errors in XRF. In general, the empirical calibration method with corrections using influence coefficients is utilized for the fusion bead method (ISO9516-1: 2003(E)). In this case, effective correction coefficients can be obtained by the fundamental-parameter (FP) method. There have been reports on analysis of ores by the empirical calibration method which takes loss-on-ignition (LOI), gain-on-ignition (GOI), dilution ratios, and weight of oxidizer into consideration (Kataoka *et al.*, 1992; Homma *et al.*, 2012). However, there are few reports by the FP method despite the fact that fusion beads are suitable samples since these are homogeneous. In this report, we describe the analysis of fused beads made of metal samples by a newly developed FP method.

When metal samples undergo fusion, an oxidizing agent is added to oxidize the samples causing LOI and GOI. Elements such as carbon are volatilized during this process and LOI occurs. To accurately perform analysis with the FP method, these weight changes must be reflected accurately in the software calculation. This report describes an FP method, which takes sample weight changes such as GOI and LOI into consideration, and an example applying this method to ferroalloy samples is presented.

II. WEIGHT CHANGE OF NON-OXIDE SAMPLE IN FUSION

When non-oxide samples are fused, all metallic elements are oxidized. Therefore, actual compound and concentrations have to be interpreted in the FP method. The three important points of non-oxide sample analysis with FP method are shown below.

A. All elements in the samples are oxidized in fused bead

Compounds and concentrations as oxides have to be used in the quantification calculation. Total converted concentration as oxides exceeds 100% and gain of weight by oxidation is considered as GOI. The weight changes because of fusion including LOI, GOI, and oxidizer are illustrated in Figure 1.

B. Volatile elements such as carbon do not exist in fused bead

Concentrations of volatile elements such as carbon in ferroalloys are considered as LOI and are corrected in the FP method.

C. Concentrations as oxide components in fused bead are obtained with weight ratios of remaining oxidizer and flux to sample

The converted concentrations as oxide components in fused bead are utilized in theoretical intensity calculation in the FP method.

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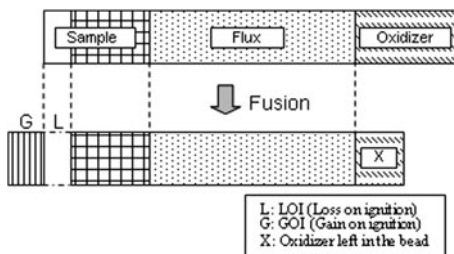


Figure 1. Weight changes in fusion.

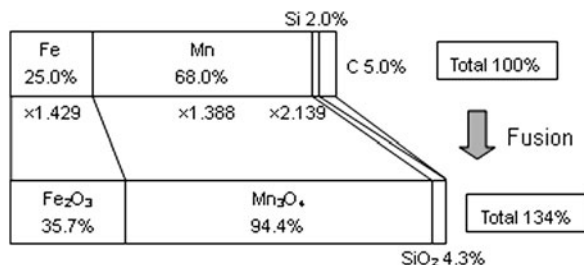


Figure 2. Concentrations as oxide based on original sample.

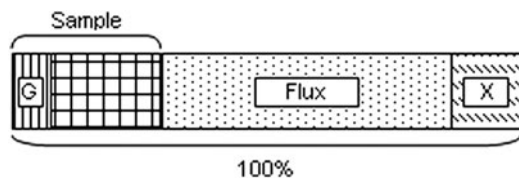


Figure 3. Concept of concentrations as oxide based on fused bead.

TABLE I. Standard reference materials.

Ferrosilicon	Ferromanganese	Silicomanganese
NCS HC14606	VS F5/3	DH SL 01-07
NIST SRM 58a	NIST SRM 68c	MHCX03
NIST SRM 59a	BAM 502-2	ECRM 586-1
BS 140-4	JSS 701-6	JSS 705-4
DH SL 23-11	NCS HC18602	DH SL 03-01
DH SL 23-12		
IPT 143		

III. QUANTIFICATION CALCULATION IN FP METHOD

There are two important calculation procedures in the FP method.

A. Concentration calculation

The concentration at which measured and theoretical intensities match are obtained iteratively in this procedure. Concentrations based on the original sample are used for quantification.

The weight of each component changes by oxidation as a result of fusion preparation. In the example in Figure 2, Fe, Mn, and Si are oxidized. In the case of Fe, the Fe₂O₃ concentration increases by a factor of 1.429–35.7%.

Carbon is volatilized and does not remain in the fused bead. It is considered as LOI. Gain of weight because of

oxidization is considered GOI and it can be considered as negative LOI. Total converted concentration as oxides exceeds 100% in non-oxide samples. It is 134% in this example. The difference between 100% and total % as oxides is the summation of LOI and GOI. Therefore, normalization of the total concentration to 100% must not be included in the concentration calculation.

B. Theoretical intensity calculation

The theoretical intensities of fluorescent X-rays are calculated for given concentrations based on fused bead. The concept of concentrations as oxides based on fused bead is shown in Figure 3.

The bead based concentrations as oxides are utilized in the theoretical intensity calculation. W_J is sample-based concentration and C_J is bead-based concentration. The three equations below are the concentrations of the sample component C_J , flux C_F , and remaining oxidizer C_X . R_X is the weight ratio of oxidizer left in the fused bead to sample, and R_F is the weight ratio of flux to sample.

$$C_J = \frac{W_J}{W_{\text{Total}} + R_X + R_F}$$

$$C_F = \frac{R_F}{W_{\text{Total}} + R_X + R_F}$$

$$C_X = \frac{R_X}{W_{\text{Total}} + R_X + R_F}$$

$$W_{\text{Total}} = \sum_{J \neq \text{LOI}} W_J$$

The important point is that W_{Total} is the summation of all oxide concentrations excluding LOI. In addition, changes in sample weight such as LOI, GOI, and oxidizer during fusion must also be considered in concentration calculation.

IV. EXPERIMENTAL

Certified reference materials (CRMs) of seven ferrosilicon (FeSi), five ferromanganese (FeMn), and five silicomanganese (SiMn) samples were used to establish the calibration. The three types of certified reference materials of ferroalloys are standards from NIST, Brammer Standard (USA), JSS (Iron & Steel Institute of Japan), BAM (Germany), AG der Dillinger Hüttenwerke (Germany), IRSID (Institut de Recherches de las Siderugie, France), NCS (China National Analysis Center for Iron and Steel), Standard Samples Office (Ukraine), Institute for Certified Reference Materials (Russia), and IPT (Brazil). The samples include both low and high carbon types of ferroalloys. Each of the CRMs was ground for 2 min using a grinding mill and tungsten-carbide container.

Since ferroalloy powders are metal, the samples cannot be fused by a conventional fusion technique. A special fusion technique was employed for this application. The sample mixture, flux (Li₂B₄O₇) and oxidation reagent were pre-oxidized in a crucible by heating at about 500–600 °C for 2 h prior to fusion. The oxidation reagent was prepared by blending Li₂CO₃, Na₂CO₃, and KNO₃ in equal weight. The weights of the flux and the mixture of the oxidation reagents were

TABLE II. Concentration ranges of standard reference materials.

Component	Ferrosilicon	Ferromanganese	Unit: mass%
			Silicomanganese
Si	48.10–78.96	0.03–2.38	14.76–30.16
Fe	9.06–50.05	2.73–12.3	2.64–9.91
Mn	0.058–1.00	64.78–95.9	59.06–77.82
Ni	0.0028–0.11	0.0384	0.014–0.11
Cr	0.0044–0.19	0.0265–0.0740	0.016–0.20
Ca	0.042–10.48	–	0.028–0.039
Al	0.24–4.36	–	0.013–0.050
Mg	0.0051–1.15	–	0.015
C	0.024–8.31	0.079–6.94	0.015–2.11

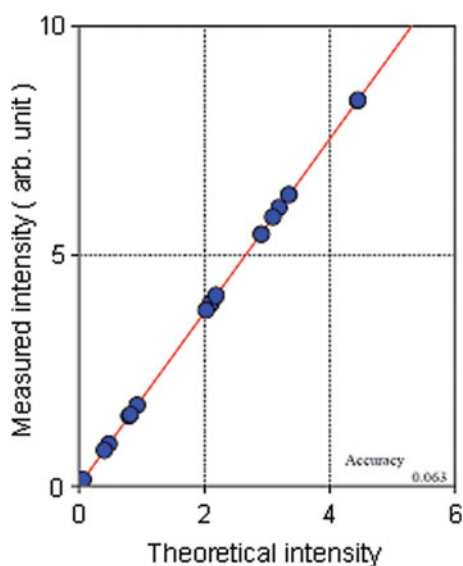


Figure 4. Sensitivity calibration of SiK α .

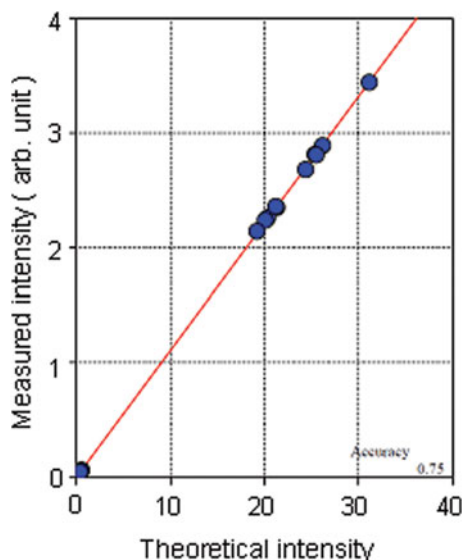


Figure 5. Sensitivity calibration of MnK α .

4.0 and 1.8 g, respectively. The sample weights for FeSi were 0.16 g (flux ratio = 25), and 0.10 g for FeMn and SiMn (flux ratio = 40). To evaluate flux ratio correction, two additional FeSi samples with 0.24 g (flux ratio = 16.7) were prepared. The fusion temperature was 1200 °C.

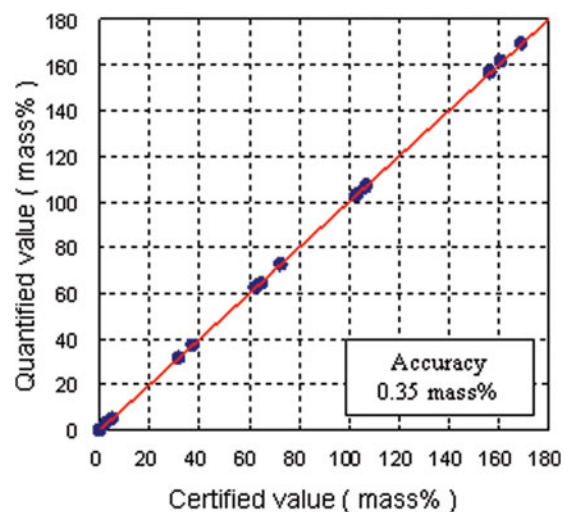


Figure 6. Relationship between certified and quantified values of SiO₂.

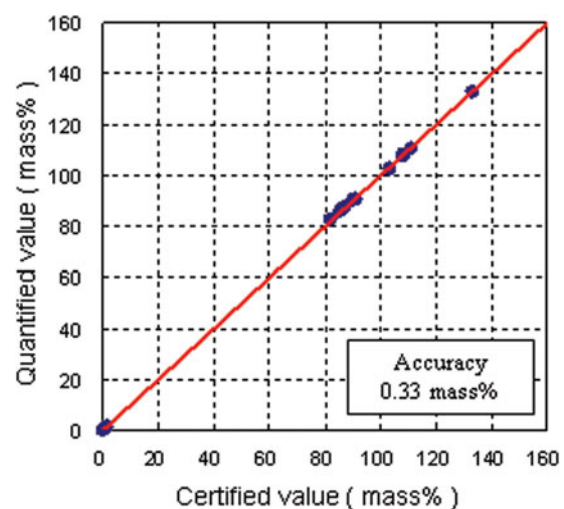


Figure 7. Relationship between certified and quantified values of Mn₃O₄.

Eight elements; Si, Mn, Fe, Ni, Cr, Ca, Al, and Mg were measured using the K α lines for all eight elements. Seventeen standard samples of three types of standard reference materials were analyzed. The materials are listed in Table I and the concentration ranges of the standard samples are tabulated in Table II.

The measurements were performed using a Rigaku sequential WDXRF spectrometer ZSX PrimusII with an Rh target end-window X-ray tube. The samples were measured at 50 kV and 60 mA for all elements. The counting time for Mg and Al is 40 s for each peak and 20 s for each of the two backgrounds. The counting time for the Fe peak is 20 s. The counting time for the other elements is 20 s for each peak position and 10 s for each of the two backgrounds.

A LiF(200) analyzing crystal was used for the elements Ca, Ti, Cr, Mn, Fe, and Ni. PET was used for Si and Al, and Ge(111) crystal was used for P. A scintillation counter was used for all the heavy elements from Ti, and a gas flow proportional counter was used for the remaining light elements.

TABLE III. Calibration accuracies of eight elements as oxides.

Component	Concentration range	Unit: mass% Accuracy
SiO ₂	0.064–168.93	0.35
Fe ₂ O ₃	3.77–71.57	0.39
Mn ₃ O ₄	0.081–133.14	0.33
NiO	0.0036–0.14	0.0099
Cr ₂ O ₃	0.0064–0.29	0.0059
CaO	0.039–14.66	0.040
Al ₂ O ₃	0.025–8.24	0.085
MgO	0.0085–1.91	0.027

TABLE IV. Calibration accuracies of eight elements as elements in ferroalloys.

Element	Concentration range	Unit: mass% Accuracy
Si	0.03–78.96	0.16
Fe	2.64–50.05	0.28
Mn	0.058–95.9	0.23
Ni	0.0028–0.11	0.0078
Cr	0.0044–0.20	0.0040
Ca	0.028–10.48	0.029
Al	0.013–4.36	0.045
Mg	0.0051–1.15	0.016

V. SENSITIVITY CALIBRATION

The sensitivity calibrations for SiK α and MnK α are shown in Figures 4 and 5. The sensitivity calibration equation is expressed by the correlation between theoretical intensity I_T and measured intensity I_M as shown below.

$$I_T = A \cdot I_M + B$$

Even though the calibrations consist of data of fused beads prepared at different flux ratios (weight ratios of flux to sample) of 16.7 and 25 for FeSi and 40 for FeMn and

SiMn, and for a wide range of concentrations, good linear relationship could be obtained.

The correlations between the quantified values by the FP method and the certified values of all three types of fused beads for FeSi, FeMn, and SiMn are shown in Figure 6 for SiO₂ and Figure 7 for Mn₃O₄. The correlations are expressed by the concentrations as oxides of SiO₂ and Mn₃O₄.

Table III lists the summary of calibration accuracies for all eight measured elements using 17 standards. The accuracy is 0.35% for SiO₂ and 0.33% for Mn₃O₄. The accuracy converted to silicon is 0.16 and 0.23% for manganese. The calibration accuracies expressed as element concentrations in ferroalloys are shown in Table IV.

VI. RESULTS

The analysis results for high carbon ferroalloys by the newly developed FP method are compared with the results obtained by an empirical calibration method in Table V. In the empirical calibration method, the alpha corrections of matrix components and flux ratio correction were applied but LOI correction was not applied. The table lists the results for three major elements of three different samples. The first sample (DH SL23-11) contains 8.31% of carbon and the third sample (DH SL01-07) was prepared by a different flux ratio of 40. The deviations in the FP method are much smaller than those for the empirical method, especially for high concentrations.

VII. CONCLUSION

The results demonstrate that the three types of ferroalloys with a wide range of compositions including high carbon ferroalloys can be accurately analyzed by the fusion method using the newly developed FP method. This method corrects for the effects of large GOI by oxidation of metallic elements and LOI by a volatile element such as carbon. This method can be applied to other non-oxide samples such as sulfides and carbides.

TABLE V. Analysis results for high carbon ferroalloys.

DH SL23-11 (High carbon ferrosilicon) C: 8.31%, Flux ratio: 25						Unit: mass%
Component	Standard value	FP method			Empirical method	
		Analyzed value	Deviation	Analyzed value	Deviation	
Si	50.00	50.08	0.08	51.92	1.84	
Fe	9.06	9.01	−0.05	9.27	0.21	
Mn	0.080	0.073	−0.007	0.133	0.053	
DH SL23-12 (High carbon ferrosilicon) C: 4.96%, Flux ratio: 25						Unit: mass%
Component	Standard value	FP method			Empirical method	
		Analyzed value	Deviation	Analyzed value	Deviation	
Si	48.30	48.25	−0.05	49.95	1.65	
Fe	12.38	12.59	0.21	12.98	0.60	
Mn	0.114	0.094	−0.020	0.155	0.041	
DH SL01-07 (High carbon silicomanganese) C: 1.65%, Flux ratio: 40						Unit: mass%
Component	Standard value	FP method			Empirical method	
		Analyzed value	Deviation	Analyzed value	Deviation	
Si	17.36	17.45	0.09	18.06	0.70	
Fe	2.64	2.54	−0.10	2.50	−0.14	
Mn	77.82	77.97	0.15	77.63	−0.19	

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